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Kenneth J. Wynne

6. AUTHOR(S)

T. Goodson, J. Takacs, C. H. Wang, and L. Zhang

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

632 Hamilton Hall
Department of Chemistry
University of Nebraska-Lincoln
Lincoln, NE 68588-0304

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The Synthesis, Characterization, and Photochemical Crosslinking of an NLO Epoxy Polymer

Theodore Goodson, James M. Takacs,* C. H. Wang,* and Lei Zhang

Department of Chemistry, University of Nebraska, LINCOLN NE 68588-0304

Abstract. A photocrosslinkable second order nonlinear optical (NLO) epoxy polymer, Bisphenol A-Nitroaminotolane, containing covalently attached cinnamate side chain substituents (BisA-NAT-CM), was synthesized. After corona poling Second Harmonic Generation (SHG) is used to measure the relaxation of the anisotropy after the electric field is removed. Upon photolysis at 260 nm the cinnamoyl-side chains undergo photochemical dimerization to crosslink the NLO polymer. Photobleaching is not a problem under these conditions. The photocrosslinked NLO polymer shows virtually no relaxation over a period of 500 hours at room temperature and good temporal stability at temperatures as high as 110 °C.

Introduction

Organic nonlinear optical (NLO) polymers are attracting much interest due to their potential advantages over inorganic crystals in electro-optic applications. Electric-field-induced alignment of the NLO chromophore by poling now quite routinely produces NLO polymers whose peak performance equals or exceeds that of state-of-the-art crystals.^{1, 2} Improving the temporal stability of poled NLO polymers, particularly at elevated temperatures, remains an important challenge. Herein, we report the full details of our study into a functionalized epoxy polymer that is efficiently photocrosslinked. After electric field poling, the aligned polymer film exhibits good temporal stability of the SHG intensity at temperatures up to 110 °C. This study illustrates an example of the photochemical crosslinking of an NLO polymer wherein the polymer is stable toward photobleaching under the UV photolysis conditions.

Attempts to prepare polymers with large and stable second-order NLO effects are largely

focused on the preparation of high T_g polymers and polymer guest-host systems.³ Among the known classes of high T_g linear polymers, the polyimide and polyetherimide polymers are attracting particular attention due to their current utility in the electronics industry.^{4,5} For example, Stahelin and co-workers⁶ at IBM recently reported excellent stability for a processible guest-host polyimide system. However as the weight percent of NLO chromophore in the guest-host system is increased, T_g decreases significantly.⁷ Marks and co-workers⁸ reported a covalently functionalized polyimide that exhibits excellent temporal stability, but as is often the case, the functionalized polyimide is apparently only processible at the polyamic acid stage.

Three dimensional network polymers also frequently possess high T_g 's, and as such, are likely candidates for stable second-order NLO effects. Relatively early on, a three-dimensional network epoxy polymer was prepared by the IBM group⁹ by adding a diamino-functionalized NLO chromophore to a bisepoxide monomer. Films were prepared from a low molecular weight prepolymer and the network polymerization completed under conditions of poling the film. The resulting film exhibited excellent temporal stability of the electro-optic response, however, this approach is complicated by the need for a processible prepolymer and the difficulty in controlling the degree of subsequent polymerization during poling of the film. However, the basic approach has been further refined by Dalton¹⁰ and by Francis and coworkers.¹¹ These latter workers reported formation of a novel thermally crosslinked polyurea-polyurethane via the reaction of a bifunctional NLO chromophore with a triisocyanate monomer. The aminoalcohol chromophore initially reacts through the amino functionality to afford largely a linear polyurea which upon heating under the conditions of poling crosslinks via urethane formation between the less reactive hydroxyl group on the chromophore with the residual isocyanate. Marks and co-workers^{12, 13} reported the chemical cross-linking of an NLO polymer by subsequent treatment of the hydroxy-containing NLO polymer with a bis-epoxide crosslinking agent.

An alternative approach to the synthesis of three-dimensional network polymers is based on the photocrosslinking of suitably functionalized linear polymers during or after poling. The conditions required for photochemical crosslinking may be more suitable to device applications

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than chemical crosslinking methods. Several guest-host polymer systems that are stabilized by photocrosslinking have been reported.¹⁴⁻²⁰ Recently, Tripathy and co-workers²¹ communicated the results of a study of four photocrosslinked polymer systems, one wherein the NLO chromophore (4-nitroaniline) and the photocrosslinking moiety (cinnamate) are covalently appended to an epoxy polymer backbone (bisphenol A diglycidyl ether). We have also been interested in the optical properties of NLO epoxy polymers,²²⁻²⁵ and now wish to report the full details of our study of a polymer system closely related to that of Tripathy, a cinnamate-functionalized epoxy polymer (BisA-NAT-CM) derived from the combination of bisphenol A diglycidyl ether, 4,4'-nitroaminotolane and cinnamoyl chloride.

Experimental

Bisphenol A diglycidyl ether was purchased from Monomer-Polymer & DAJAC Laboratories, Inc. 4,4'-Nitroaminotolane (NAT) is prepared via the palladium-catalyzed coupling of 4-nitrophenylacetylene to 4-iodoaniline according to the method of Hagihara.²⁶

Preparation of BisA-NAT-CM. To a filtered solution (0.2 μ m) of bisphenol A diglycidyl ether (0.71 g, 2.1 mmol) in propyleneglycol monomethyl ether (PM, 3 mL) is added NAT (0.50 g, 2.1 mmol). The resulting solution is refluxed (120 °C, 24 h) under an inert atmosphere (N₂), then cooled to ambient temperature. To the resulting dark red solution is added pyridine (1 mL) and cinnamoyl chloride (0.17 g, 1.05 mmol). The molar percentage of the cinnamate added to the copolymer is 25 percent.^a The resulting mixture is stirred (24 h), and then the polymer precipitated with ether (50 mL), filtered, washed with ether (50 mL), and dried in vacuo. BisA-NAT-CM (0.84 g, 61 %) is obtained as an amber powder. GPC analysis (THF) shows a M_w of 1000 relative to polystyrene standard.

Film Preparation. The polymer is dissolved in the solvent DMSO making a 0.1 g/mL concentrated solution. Thin films are spun onto transparent conducting Indium Tin Oxide (ITO) plates. The spinning rate is 1000 rpm. The resulting thin film (~1 μ m) is then baked or cured in a vacuum oven above the glass transition temperature (150 °C, 12 hours), to remove traces of

solvent.

Photocrosslinking. The thin film sample is equilibrated at 100 ± 5 °C in an oven equipped with transparent windows and a corona poling needle. Initially, the sample is irradiated at 260 nm with a 150 watt xeon arc lamp (Photon Technology International) which is connected to a monochromator. The lamp generates a power of 1.5 - 2 mW/cm² at 260 nm. UV-Vis and refractive index analysis of the film after photolysis for two hours shows no evidence of photobleaching of the NLO chromophore. The film is then poled with an applied voltage of 3 KV with the current maintained at 0.1 - 0.3 mA. The film is irradiated and poled simultaneously at 100 °C for 5 minutes, then the temperature is slowly lowered to ambient over the course of approximately an hour at which time the lamp and electric field are switched off.

Second Harmonic Generation (SHG) Measurements. SHG measurements were performed using an apparatus similar to that reported by Guan and Wang,²⁷ and is shown in figure 1. It consists of a Spectra Physics DCR-11 Q switched ND:YAG laser with a pulse width of approximately 10 ns and 10 Hz repetition rate as the fundamental source. The film is held in a temperature controlled (± 5 °C) oven. The sample film assembly itself is mounted on a goniometer rotating stage. The optical field maintained P-polarization at an incidence angle of 50° to the polymer film surface.

Results and Discussion

Synthesis and Characterization of BisA-NAT-CM. The N,N-dimethyl derivative of 4,4'-nitroaminotolane possesses a large hyperpolarizability ($\beta = 102 \times 10^{-30}$ esu) and a large dipole moment (7.1 D),²⁸ and as such, it is an interesting NLO chromophore for incorporation in NLO polymers. The condensation of NAT with bisphenol A diglycidyl ether (scheme 1) affords the epoxy polymer BisA-NAT, for which the nonlinear optical²⁹ and electro-optical properties²³⁻²⁵ (d_{13} and r_{13}) have been studied. Cinnamate esters undergo a well-characterized [2+2]-dimerization under conditions of UV photolysis, and we chose this process as the vehicle for preparing a photocrosslinkable NLO polymer. In order to maximize the number density of the NAT

chromophore, the BisA-NAT epoxy polymer was treated with just 0.25 equivalents (based upon the calculated number of available free hydroxyl groups) of cinnamoyl chloride. The resulting cinnamate-functionalized epoxy polymer (BisA-NAT-CM) gives a ^{13}C NMR spectrum (figure 2) consistent with the assigned structure. The bottom full spectrum shows the BisA-NAT copolymer without cinnamate. The three insets (A-C) in figure 2 show expanded regions highlighting the characteristic spectral changes upon the covalent attachment of 0.0 (inset A), 0.25 molar equivalents (inset B) and 1.0 molar equivalents (inset C) of cinnamate to the BisA-NAT copolymer. The 0.25 molar equivalents BisA-NAT-CM polymer shown in inset B was used in the photocrosslinking studies.

Thermogravimetric analysis of the BisA-NAT-CM polymer were performed to estimate the thermal stability of the individual components of the polymer. The first derivative curve indicated three apparent modes of decomposition. An initial decrease near 240 °C can be attributed to decomposition of the NLO chromophore, NAT. The next drop is seen near 280 °C and may be due to the loss of cinnamate groups. Finally, a drop at 360 °C is characteristic of the degradation of the polymer main chain. All poling and curing of the BisA-NAT-CM polymers were performed at temperatures below 240 °C, a temperature at which all components are stable.

Calorimetric studies were performed on the cured polymer thin film before and after photolysis. The DSC trace for BisA-NAT-CM (10 °C/min) shows a distinctive glass transition step at 80 °C. Upon photolysis (260 nm, 2 mW/cm²) the DSC trace changes, and after two hours of photolysis, the measured T_g is increased to 120 °C. This increase in T_g is consistent with a significant extent of photocrosslinking.^b

Linear Optical Properties. The refractive index was determined from measurements of the coupling angles for the transverse electric (TE) mode in the slab waveguide configuration (Metricon prism coupling instrument). A sequence of minima in the observed reflectivity as a function of angle due to excitation of transverse modes in the polymer film ($\lambda = 632.8$ nm, TE polarization) is obtained. The pristine BisA-NAT-CM sample showed a refractive index of 1.6280

and a film thickness of 0.7543 μm . Dalton and co-workers¹⁷ found a decrease in the refractive index upon photolysis of an azo dye-based photocrosslinkable NLO polymer system at wavelengths above absorption. This photobleaching process has been suggested as a potential technique for the fabrication of optical waveguides,^{30, 31} and Hayashi and co-workers³² recently prepared a photoactivated NLO polymers based on a similar idea. In the present case however, photocrosslinked BisA-NAT-CM shows only negligible changes in the refractive index.

Second Harmonic Generation. To probe the dipolar orientational relaxation of the photocrosslinked BisA-NAT-CM polymer, second harmonic generation (SHG) measurements were made.³³ The time dependence of the SHG signal for the pristine BisA-NAT-CM polymer is shown in figure 3. The sample was poled at 80 °C (*i.e.*, near the measured T_g) with an applied corona field of 3 kV. The intensity of the observed SHG signal rises sharply, however, at 80 °C the signal relaxes rapidly and approaches background levels within about 1000 sec when the poling field is turned off. At this temperature, the temporal stability of the electric field induced alignment in the pristine BisA-NAT-CM film is less than that reported for the better guest host systems.^{6, 34,}³⁵ The pristine BisA-NAT-CM polymer can be re-poled with the SHG signal intensity rising sharply to approximately the same initial value and relaxing over about the same time span.

As expected the temporal stability of the SHG signal is dramatically increased upon photolysis of the BisA-NAT-CM film (80 °C, 260 nm, 2 mW/cm², see experimental section for details). After photolysis, the SHG signal intensity of the photocrosslinked film, monitored at ambient temperatures over the course of 500 hours (figure 4), show an initial 3-5 % decrease in intensity then remains essentially constant over that time frame. At 80 °C, the SHG also remains fairly stable (figure 3). We observe a 10-15 % decrease in signal intensity over the course of 5000 seconds. Recall that in the pristine film, the SHG signal decays to background within 1000 seconds (80 °C). At 110 °C, a temperature approximately 10 °C below T_g for the photocrosslinked polymer, we observe a 20-25 % decrease in signal intensity over the course of 5000 seconds. Attempts to enhance the dipolar alignment and/or re-pole the crosslinked copolymer at elevated temperature (80 °C) show no increase in SHG signal intensity upon re-application of the corona

field.

Conclusions. Cinnamate-functionalized epoxy polymers afford photocrosslinked NLO polymers exhibiting good temporal stability at elevated temperatures (80 - 110 °C). These results complement those recently reported by Tripathy and co-workers,²¹ who show good temporal stability for a cinnamate photocrosslinked polymer at ambient temperature. In our system, the crosslinking agent is required in only relatively small amounts. We see no evidence for detrimental effects due to photobleaching, an effect which is observed in the case of some azo dye systems.¹⁷ We also note that the observed SHG decay is reversible for the non-crosslinked polymer, while the crosslinked polymer showed no change due to re-poling at elevated temperatures.

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Footnotes

- ^a A second BisA-NAT-CM polymer, one in which the molar percentage of the cinnamate added to the copolymer was 100 percent, was prepared as a reference material for spectroscopic characterization (*vide infra*).
- ^b GPC analysis of a soluble portion of polymer after photolysis, indicates a M_w of approximately 2.5×10^4 relative to polystyrene.

Scheme 1. Preparation of pristine and photocrosslinked BisA-NAT-CM.

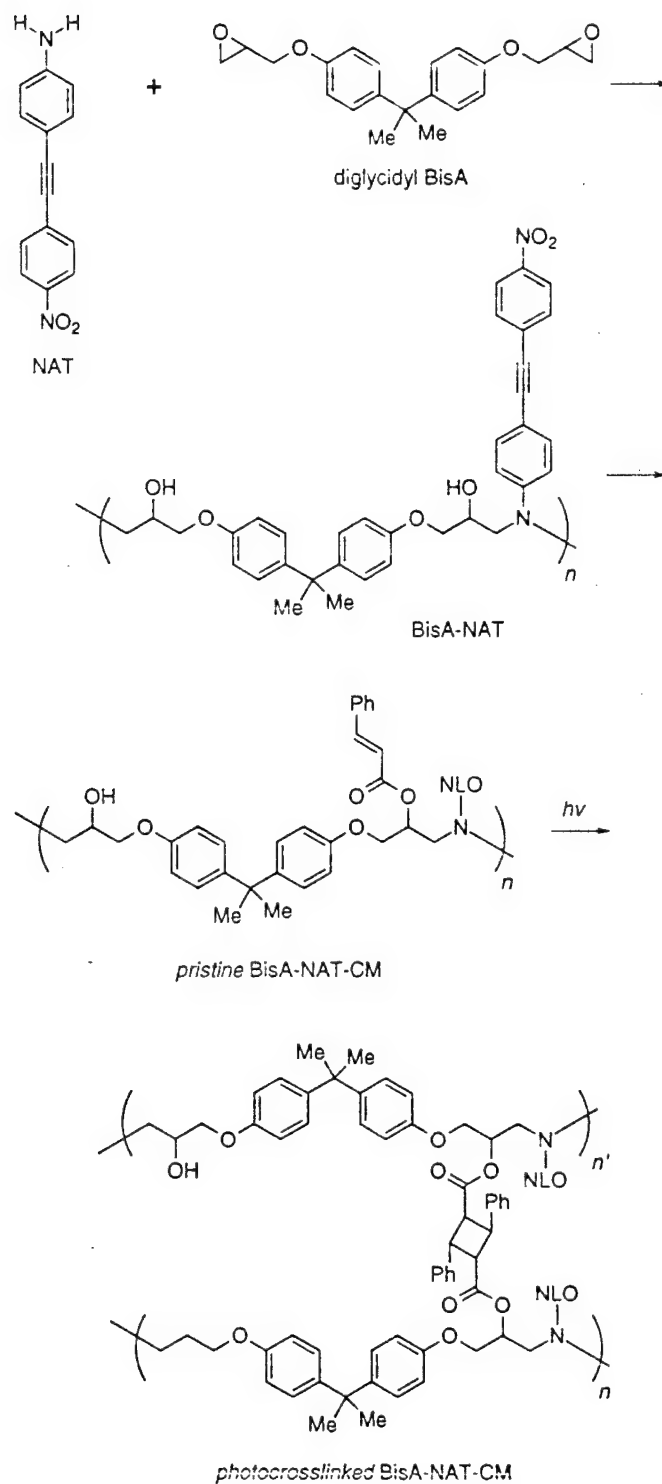
Figure 1. Apparatus for SHG measurements. Symbols R and S refer to reference and sample, respectively. PC is personal computer and PMT is a photomultiplier tube. SHC is a second harmonic crystal. The other notations are self-explanatory.

Figure 2. Comparison of the 75 MHz ^{13}C NMR spectra (methyl sulfoxide- d_6) of BisA-NAT (inset A), BisA-NAT-CM (0.25 molar equivalents cinnanmate, inset B) and BisA-NAT-CM (1.0 molar equivalents cinnanmate, inset C).

Figure 3. The time dependence of the SHG signal for pristine BisA-NAT-CM at 80 °C and for photocrosslinked BisA-NAT-CM at 80 and 110 °C.

Figure 4. The time dependence of the SHG signal for photocrosslinked BisA-NAT-CM at ambient temperature.

Scheme 1.



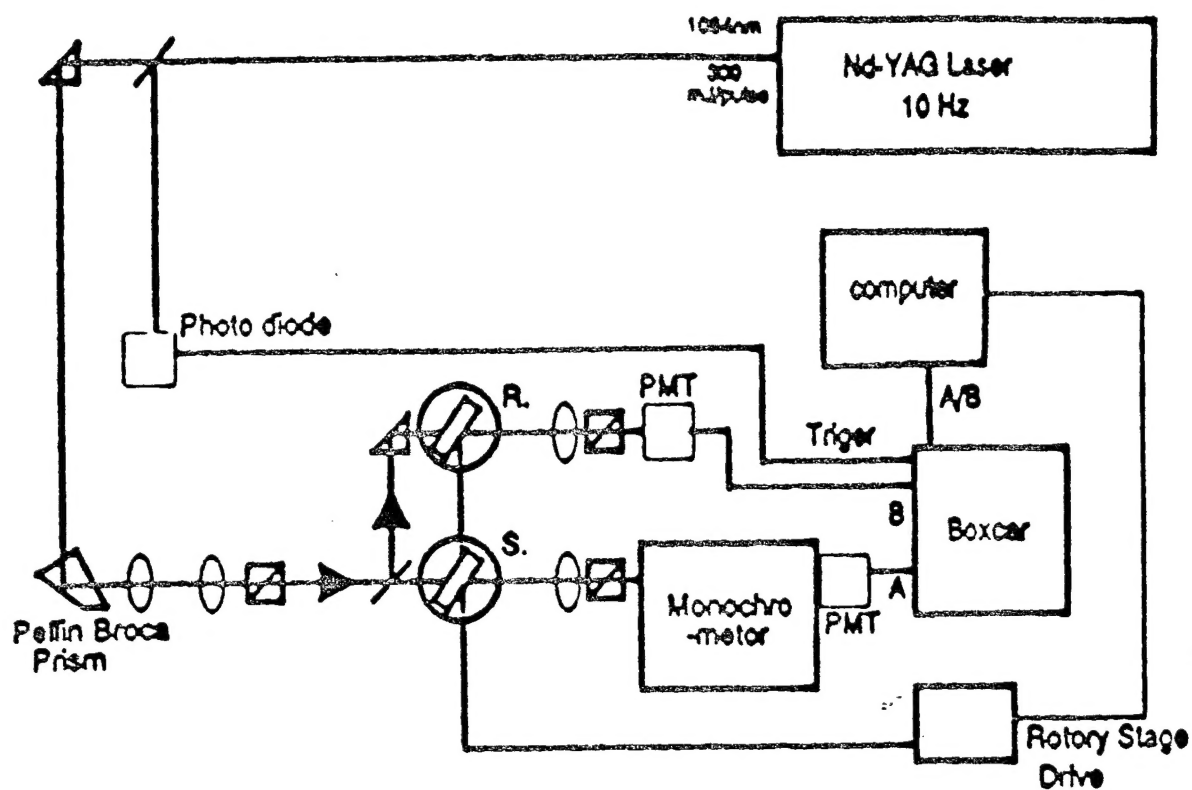
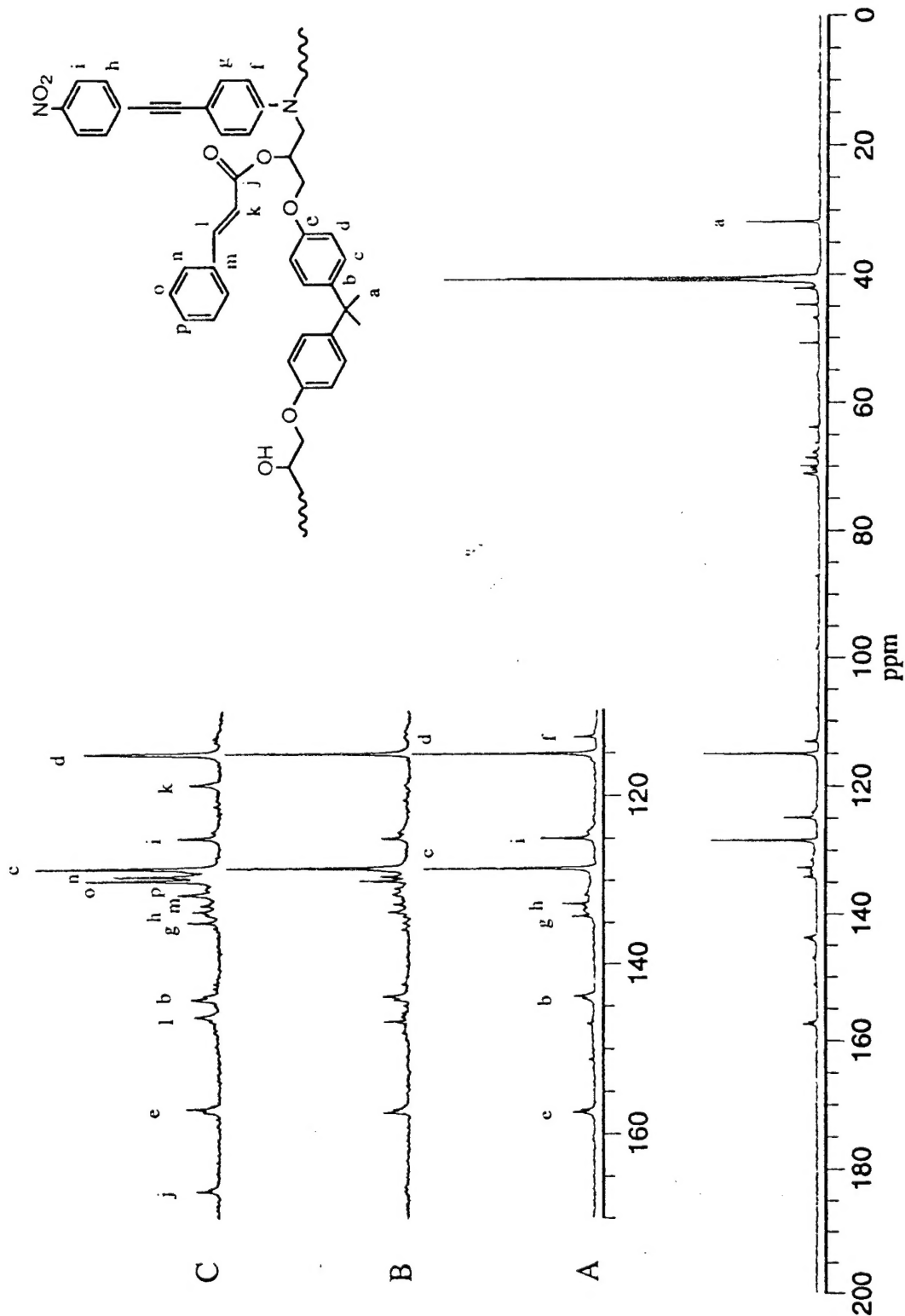
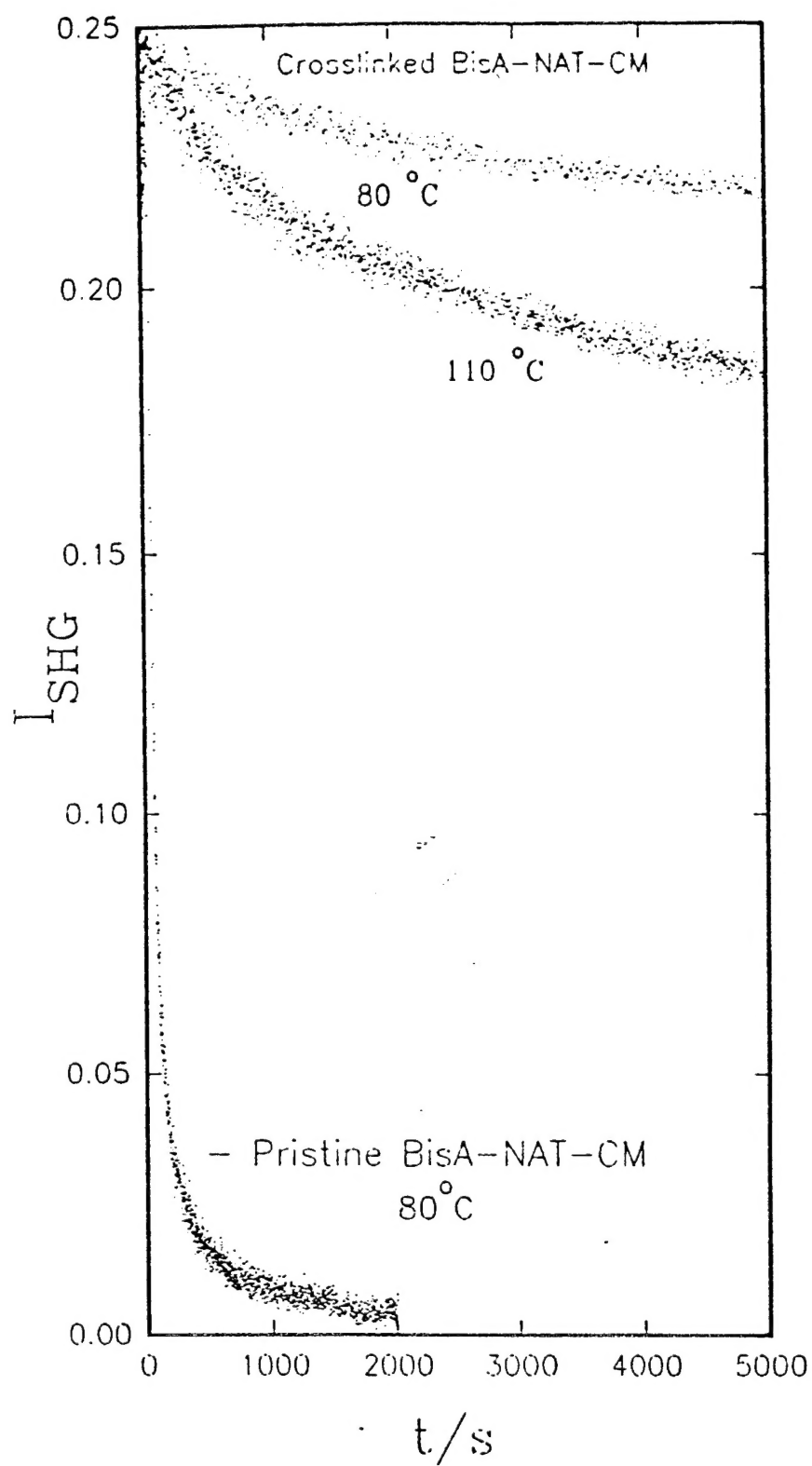


Figure 1





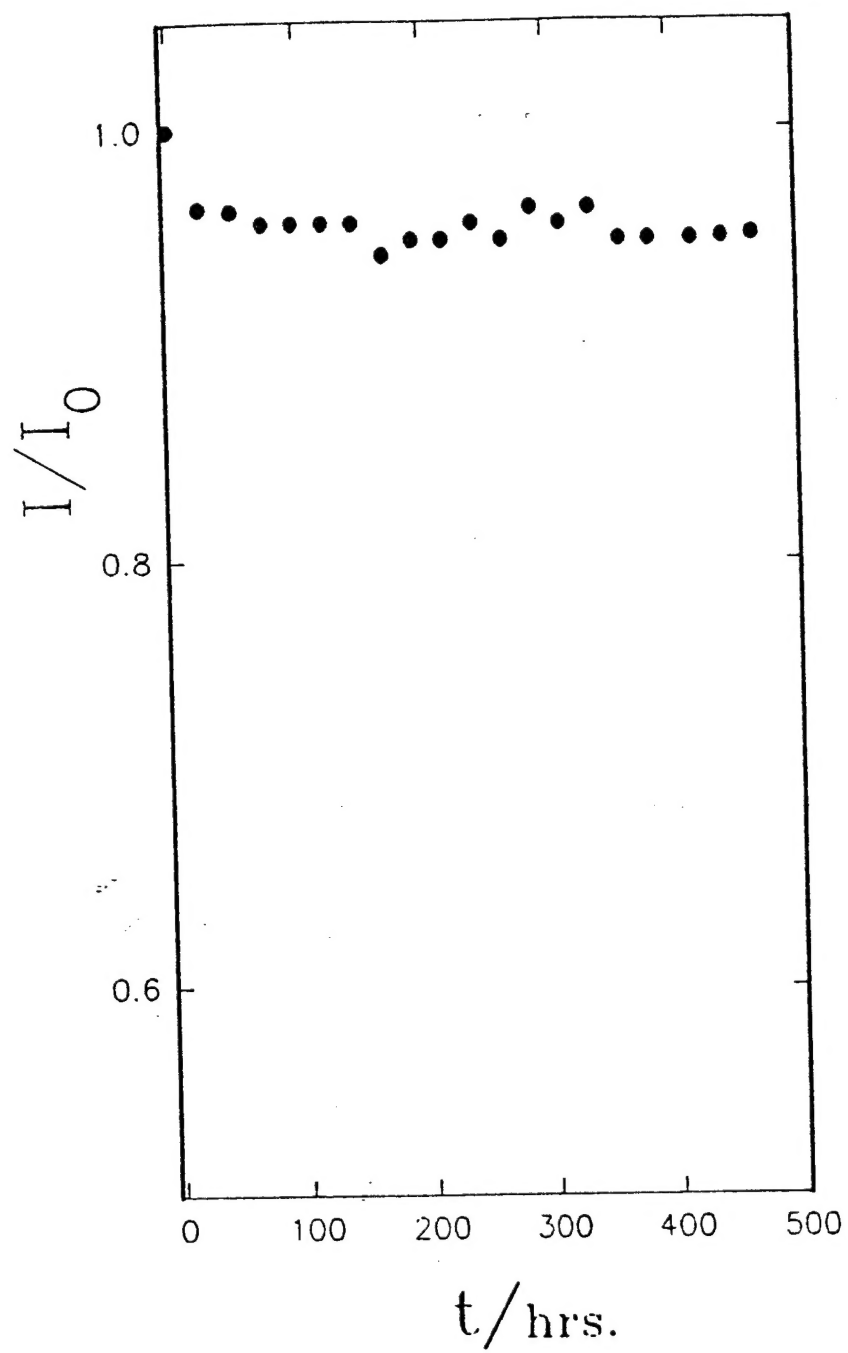


figure 4

5000 YPMO